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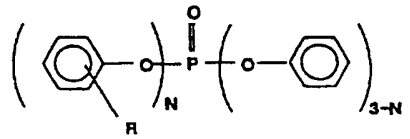
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(54) Abstract Title
Flame-retardant thermoplastic resin compositions

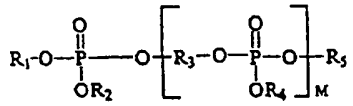
(57) Flame-retardant thermoplastic resin compositions comprise a polycarbonate, a styrene-containing graft copolymer and a mixture of alkyl-substituted monophosphate esters of formula (I):



(I)

in which:
R is an alkyl group selected from t-butyl, isopropyl, isobutyl, isoamyl, t-amyl, and
N is 0 or an integer from 1 to 3.

The composition may also contain a phosphate ester of formula (II):



(II)

in which:
R_1, R_2, R_4, and R_5 are independently cresyl, phenyl, xylenyl, propylphenyl, butylphenyl, or brominated or chlorinated derivatives thereof,
R_3 is an arylene group, and
M is 0 to 5,
a styrene-containing copolymer and a fluorinated polyolefin.

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THERMOPLASTIC RESIN COMPOSITION

The present invention relates to flame-retardant thermoplastic resin compositions. More particularly, the present invention relates to the thermoplastic resin compositions which comprise a polycarbonate, a styrene-containing graft copolymer, a styrene-containing copolymer, a mixture of alkyl substituted, preferably t-butyl substituted, monophosphate esters, a phosphate ester compound, and a fluorinated polyolefin, whose stress cracking resistance and flame retardancy are improved.

Polycarbonate resin compositions are widely used for parts of electrical products and automotive-components because they have a good combination of transparency, high impact strength, and heat resistance. However, polycarbonate resin compositions have poor processability during molding process, so polycarbonate resin compositions are usually blended with other resins for improving these properties. For example, a molding composition comprising a polycarbonate resin and a styrenic resin has good processability as well as high notched impact strength.

Furthermore, the polycarbonate molding composition used for parts of home and office appliances should be flame resistant to prevent fires.

To confer flame retardancy to thermoplastic molding compositions, halogen and/or antimony containing-compounds have been incorporated. In U.S. Patent Nos. 4,983,658 and 4,883,835, a halogen-containing compound is used as a flame retardant. The halogen-containing compound, however, results in corrosion of the mold itself by the hydrogen halide gases released during a molding process and is fatally harmful due to the toxic gases liberated in the case of fire.

As a method for conferring flame-retardancy without using a halogen-based flame retardant, a method using a phosphate ester-based flame retardant is commonly used. The use of halogen-free phosphate ester compound as flame retardants avoids the problems caused by the corrosive and harmful by-products of halogen-based flame retardants. However, the phosphate ester-based flame retardants have tendency to cause deterioration of heat resistance, occurring of stress crack by volatilization of a flame retardant, and juicing during a molding process.

As a method for overcoming these problems, Japanese Patent Publication No. (Sho)62-25706 describes the use of a mixture of an arylphosphate ester prepared by reacting a phosphorus oxychloride with a divalent phenol and a monovalent phenol, and an oligomeric phosphate ester as a flame retardant. However, in this method, the flame retardant prepared by such method results in the corrosion of the mold itself by a phosphorus oxychloride and a residual metal ion derived from a metal salt used as a catalyst such as aluminum chlorides, magnesium chlorides, and so on.

U.S. Patent Nos. 5,061,745 and 5,030,675 describe polymer blends prepared from an aromatic polycarbonate, an ABS graft copolymer, a styrene containing copolymer, a monophosphate ester such as triphenylphosphate(TPP) as flame retardants, and a fluorinated polyolefin. However, the low stress cracking resistance of these molding compositions often restricts the application of non-

halogen-PC/ABS in the field of making parts of electronic and electric products, especially thin-walled parts. And heat resistance of these blends also deteriorates substantially.

In order to reduce the occurrence of stress cracking and deterioration of heat resistance by the use of a monophosphate ester, U.S. Patent No. 5,204,394 describes a polymer mixture comprising an aromatic polycarbonate, a styrene–containing copolymer and/or a styrene-containing graft copolymer and an oligomeric phosphate as a flame retardant. In this polymer mixture, it is possible to obtain a V-O rating according to UL-94 using by the oligomeric phosphate whose condensation degree is about 1.4. However, if the condensation degree of the oligomeric phosphates exceed 2.8, the flame retardancy of this polymer mixture decreases rapidly to HE rating and stress cracking resistance of the mixture also decreases.

U. S. Patent No. 5,672,645 describes flame retardant polycarbonate/ABS molding compounds whose stress cracking resistance is improved by a combination of additives comprising a monomeric phosphorus compound and an oligomeric phosphorus compound as compared with the molding compounds comprising only a monophosphorus compound or an oligomeric phosphorus compound, respectively. However, the heat resistance and stress cracking resistance of these compounds are not sufficient, so an improvement is required.

U.S. Patent No. 5,206,404 describes compositions of alkylated triphenyl phosphate esters comprising 1 to 20% by weight trialkylphenyl phosphate, 10 to 50% by weight dialkylphenyl monophenyl phosphate, 15 to 60% by weight monoalkylphenyl diphenyl phosphate and less than 2% by weight triphenyl phosphate. However, this publication contains no indication of any improvement in stress cracking resistance and flame retardancy of thermoplastic resin

compositions by adding these mixtures of triaryl phosphate esters.

The present invention is based on the discovery that flame retardant thermoplastic resin compositions with excellent stress cracking resistance and heat-resistance may be produced by adding flame retardants comprising a phosphate ester and a mixture of alkyl substituted, preferably t-butyl substituted, monophosphate esters of U.S. Patent No. 5,206,404. The flame retardant thermoplastic resin compositions of this invention have good stress cracking resistance and elevated heat resistancy as compared with the molding compound of U.S. Patent No. 5,672,645 comprising a monophosphorus compound and an oligomeric phosphorus compound as a flame retardant.

An object of the present invention is to provide a flame-retardant thermoplastic resin composition with excellent stress cracking resistance and improved heat resistance which comprises a polycarbonate, a styrene-containing graft copolymer, a styrene containing copolymer, a mixture of alkyl substituted, preferably t-butyl substituted, monophosphate esters, a phosphate ester, and a fluorinated polyolefin.

The present invention relates to thermoplastic resin compositions comprising:

(A) 40 to 95 parts by weight of a halogen-free, thermoplastic polycarbonate;

(B) 5 to 50 parts by weight of a styrene-containing graft copolymer prepared by grafting (B-1) onto (B-2) :

(B-1) 5 to 95% by weight, based on (B), of a mixture of :

(B-1.1) 50 to 100% by weight of styrene, α-methyl styrene, ring-substituted styrene, methyl methacrylate or a mixture thereof, and

(B-1.2) 50 to 0% by weight of acrylonitrile, methacrylonitrile, C_1-C_8 alkyl methacrylate, C_1-C_8 alkyl acrylate, maleic anhydride, N-substituted maleimide, or a mixture thereof;

(B.2) 95 to 5% by weight, based on (B), of a rubber with a glass transition temperature(Tg) of below -10℃ and selected from the group consisting of butadiene rubbers, acryl rubbers, ethylene/propylene rubbers, styrene/butadiene rubbers, acrylonitrile/butadiene rubbers, butadiene/styrene rubbers, polyisoprene, EPDM (ethylene-propylene-diene terpolymer) rubbers, polyorganosiloxane, and mixtures thereof;

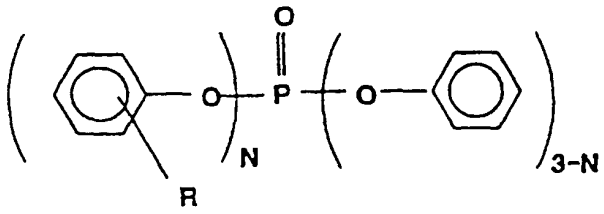
(C) 0 to 30 parts by weight of a styrene-containing copolymer prepared from:

(C-1) 50 to 95% by weight of styrene, α-methyl styrene, ring-substituted styrene, methyl methacrylate or a mixture thereof, and

(C-2) 50 to 5% by weight of acrylonitrile, C_1-C_8 alkyl methacrylate, C_1-C_8 alkyl acrylate, or a mixture thereof;

(D) 5 to 20 parts by weight, based on 100 parts by weight of (A)+(B)+(C), of a mixture comprising

(D-1) 100 to 5% by weight of a mixture of alkyl substituted, monophosphate esters of the formula (I):



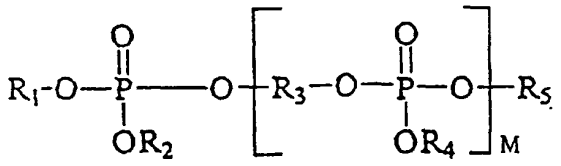
(I)

in which:

R is an alkyl group selected from t-butyl, isopropyl, isobutyl, isoamyl and t-amyl, and

N is 0 or an integer from 1 to 3, and

(D-2) 0 to 95% by weight of phosphate esters of the formula (II):



(II)

in which:

R_1, R_2, R_4, and R_5 are independently cresyl, phenyl, xylenyl, propylphenyl, butylphenyl, or brominated or chlorinated derivatives thereof,

R_3 is an arylene group, and

M is 0 to 5; and

(E) 0 to 2 parts by weight, based on 100 parts by weight of (A)+(B)+(C), of a fluorinated polyolefin polymer.

In addition to the components mentioned hereinbefore, the thermoplastic resin compositions according to the present invention may further contain one or more conventional additives. For example, inorganic fillers such as mica, talc, zeolite, and montmorillonite, pigments, dyes, glass fibers, carbon fibers, thermal stabilizers,

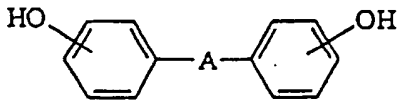
light stabilizers, antioxidants, plasticizers, and mold release agents may be added in fabrications as needed.

The thermoplastic resin compositions according to the invention comprise a polycarbonate, a styrene containing graft copolymer, a styrene containing copolymer, a mixture of alkyl substituted monophosphate esters, a phosphate ester compound and a fluorinated polyolefin polymer.

Hereinafter the detailed description regarding the respective components is provided.

(A) Thermoplastic, Halogen-free Polycarbonates

Suitable component (A) thermoplastic halogen-free polycarbonates according to the invention are those generally prepared by reacting with a phosgene or a carbonic diester, bisphenols of the following formula (III):



(III)

in which:

A is a single bond, C_1-C_5 alkylene, C_2-C_5 alkylidene, C_5-C_6 cycloalkylidene, -S- or -SO_2-.

Suitable diphenols of the formula (III) are, for example,

4,4'-dihydroxybiphenyl, 2,2-bis-(4-hydroxyphenyl) propane, 1,1-bis-(4-

hydroxyphenyl) cyclohexane, and the like. The most preferred and widely used thermoplastic, halogen-free polycarbonates are aromatic polycarbonates synthesized from 2,2-bis(4-hydroxy-phenyl)propane, called "Bisphenol A".

The production of the polycarbonates of component (A) suitable for use in accordance with the invention is known from literature, for example U.S. Patent No. 3,169,121, and may be carried out in a known manner from bisphenols with phosgene using the phase interface process or with phosgene using the homogeneous phase process.

Preferred polycarbonates according to the present invention have average molecular weights (M_w as measured for example by ultracentrifugation or by scattered light measurement) of from 10,000 to 500,000 and preferably from 18,000 to 300,000. Polycarbonates with a certain molecular weight may be obtained by using a monophenol such as phenol, paracresol, or paraisooctylphenol as chain terminator. The polycarbonates suitable for use in accordance with the invention include both homopolycarbonates and copolycarbonates.

In the present invention, the polycarbonate resins(A) comprise a base resin along with styrene containing graft copolymers and styrene containing copolymers.

(B) Styrene containing graft copolymer

Styrene containing graft copolymer which may be used according to the invention are those prepared by grafting constituent (B-1) onto (B-2):

(B-1) 5 to 95% by weight, based on (B), of a mixture of:

(B-1.1) 50 to 100% by weight of styrene, α-methyl styrene, ring-substituted styrene, methyl methacrylate or a mixture thereof, and

(B-1.2) 50 to 0% by weight of acrylonitrile, methacrylonitrile, C_1-C_8 alkyl

methacrylate, C_1-C_8 alkyl acrylate, maleic anhydride, N-substituted maleimide or a mixture thereof;

(B.2) 95 to 5% by weight, based on (B), of a rubber having a glass transition temperature(Tg) of below -10℃ and selected from the group consisting of butadiene rubbers, acryl rubbers, ethylene/propylene rubbers, styrene/butadiene rubbers, acrylonitrile/butadiene rubbers, butadiene/styrene rubbers, polyisoprene, EPDM rubbers, polyorganosiloxane, and mixtures thereof. Particularly preferred styrene containing graft copolymer(B) is the so-called ABS resin.

The preferred average particle size of the rubber is from 0.05 to 4㎛ in order to improve the impact strength and the appearance of the moldings.

The styrene containing graft copolymers of component (B) may be prepared according to conventional methods of preparing copolymer, in particular, emulsion, suspension, solution or bulk polymerization. Preferred method for preparing the graft copolymer (B) is emulsion or bulk process.

(C) Styrene containing copolymers

The styrene containing copolymers of component (C) to be used in accordance with the invention are those prepared from: (1) 50 to 95% by weight of styrene, α-methyl styrene, ring-substituted styrene, methyl methacrylate or a mixture thereof(C-1), and (2) 50 to 5% by weight of acrylonitrile, C_1-C_8 alkyl methacrylate, C_1-C_8 alkyl acrylate, or a mixture thereof(C-2).

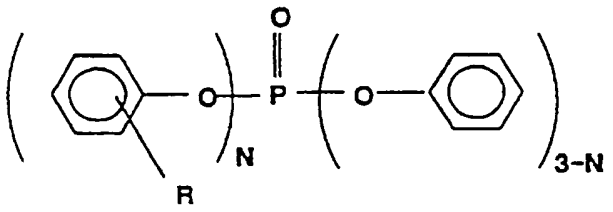
A specific example of the styrene containing copolymer is SAN(styrene/acrylonitrile) resin, which is prepared by copolymerizing styrene and acrylonitrile. In the copolymerization, 60 to 90% by weight of styrene and 40 to 10% by weight of acrylonitrile are used.

The styrene containing copolymer of component (C) may be prepared by

conventional copolymerization processes, in particular, by suspension or bulk polymerization.

(D-1) A mixture of alkyl substituted monophosphate esters

The thermoplastic resin compositions according to the present invention contain as a flame retardant a mixture of alkyl substituted monophosphate esters(D-1), and a phosphate ester compound(D-2). Component (D-1) is a mixture of alkyl substituted monophosphate esters of the following formula (I):



(I)

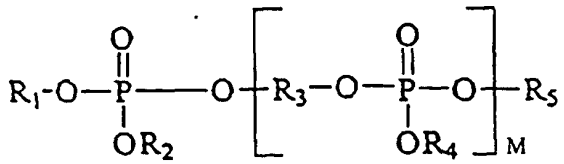
in which:

R is an alkyl group selected from t-butyl, isopropyl, isobutyl, isoamyl, t-amyl, and N is 0 or an integer from 1 to 3.

Preferably, the component (D-1) is a mixture of alkyl substituted monophosphate esters comprising by weight; 1 to 20% trialkylphenyl phosphate(N=3), 10 to 50% dialkylphenyl monophenyl phosphate(N=2), 15 to 60% monoalkylphenyl diphenyl phosphate(N=1) and less than 2% triphenyl phosphate(N=0). The preferred substituent R is t-butyl and isopropyl. The most preferred substituent R is t-butyl. A mixture of the mixed t-butylphenyl phosphate esters and the mixed isopropylphenyl phosphate esters are also preferrable.

(D-2) Phosphate Esters

The phosphate esters according to the invention have the following formula (II):



(II)

in which,

R_1, R_2, R_4, and R_5 are independently halogen-free phenyl group or C_1- C_4 alkylated aryl group,

R_3 is an arylene group, and

M is 0 or an integer from 1 to 5.

In the formula, the compound of which M is 0, is a usual monomeric phosphate ester (herinafter referred to as compound group D-2.1) and the compound of which M exceeds 0, is an oligomeric phosphate compound (hereinafter referred to as compound group D-2.2). That is, the phosphate-based flame retardant useful in the thermoplastic resin compositions according to the present invention comprises compounds of the formula (II) having M values from 0 to 5.

Preferred substituents R_1, R_2, R_4, and R_5 are independently one of cresyl, phenyl, xylenyl, propylphenyl, butylphenyl, and brominated or chlorinated derivatives thereof. R_3 is derived from diphenols such as, for example, bisphenol A, resorcinol or hydroquinone. Examples of preferred phosphate esters are a phosphate ester such as triphenyl phosphate, tri(2,6-dimethylphenyl) phosphate, tri(4-methylphenyl) phosphate, tricresyl phosphate, diphenylcresyl phosphate, tri(isopropylphenyl) phosphate, trixylenyl phosphate, xylenyldiphenylphosphate, an oligomeric phosphorus compound thereof, or mixtures of these compounds.

The thermoplastic resin compositions according to the invention contain a mixture of (D-1) and (D-2) as a flame retardant. The weight ratios of (D-1) and (D-2) may be varied within a wide range. The weight ratio of (D-1) to (D-2) is

preferably between 100:0 and 5:95, more preferably between 80:20 and 5:95 and most preferably between 55:45 and 15:85.

(E) Fluorinated Polyolefin

Preferred fluorinated polyolefins (E) are polytetrafluoroethylene, polyvinylidene fluoride, tetrafluoroethylene/vinylidene fluoride copolymer, and tetrafluoroethylene/hexafluoropropylene copolymer. These fluorinated polyolefins may be used alone or in admixture with two or more other fluorinated polyolefins. These polymers may be produced by known processes, such as for example, by polymerization of tetrafluoroethylene in an aqueous medium with a free radical forming catalyst.

The use of fluorinated polyolefins decreases flow viscosity of the thermoplastic resin composition and increases coefficient of shrinkage of the composition by forming a fibrillar network during extruding, threreby reducing or preventing the dripping of the melting resin.

The fluorinated polyolefins may be used in powder form or in emulsion form. Fluorinated polyolefins of emulsion form have good dispersibility, but make the preparation process complicated. Threrefore, it is desired to use powder form fluorinated polyolefins capable of being dispersed evenly in the total resins and forming fibrillar network.

The fluorinated polyolefin suitable for use in accordance with the invention is polytetrafluoroethylene. Polytetrafluoroethylene with an average particle size of 0.05 to 1,000㎛ is suitable for blending.

0 to 2.0 parts by weight of a fluorinated polyolefin polymer, based on 100 parts by weight of the base resin (A)+(B)+(C) is blended.

Conventional Additives

In addition to the above-mentioned constituents, the thermoplastic resin compositions according to the invention may further contain one or more other conventional additives. For example, inorganic fillers, thermal stabilizers, antioxidants, light stabilizers, plasticizers, pigments, dyes, and mold releasing agents may be added. The content of these conventional additives may be 0 to 50 parts by weight based on 100 parts by weight of the base resin (A)+(B)+(C).

The thermoplastic resin compositions are prepared according to the conventional techniques of preparing resin compositions, for example, by mixing together the constituents including the various additives and melt-extruding with extruders in pellet form.

Following are examples which illustrate procedures including the best mode for practising the invention. They are not to be construed to limit the scope of the invention defined by the appended claims in any manner whatsoever. All percentages are by weight unless otherwise noted.

The following constituents were used in the examples hereinafter:

(A) Polycarbonate

Polycarbonate of Bisphenol A having a weight average molecular weight of 20,000 was used.

(B) Styrene-containing graft copolymer (ABS)

45 parts by weight of butadiene latex in powder, 36 parts by weight of styrene, 14 parts by weight of acrylonitrile, and 150 parts by weight of deionized water were

mixed, and 1.0 parts by weight of potassium oleate, 0.4 parts by weight of cumene hydroperoxide, and 0.3 parts by weight of mercaptan-based chain transfer agent were added to the mixed solution. The resulting solution was kept at 75℃ for 5 hours to prepare a graft ABS(g-ABS) latex. To the resulting graft copolymer, 1% sulfuric acid solution was added to prepare ABS resin in powder.

(C) Styrene-containing copolymer(SAN)

To a mixed solution of 70 parts by weight of styrene, 30 parts by weight of acrylonitrile and 120 parts by weight of deionized water, 0.2 parts by weight of azobis(isobutyronitrile) and 0.5 parts by weight of tricalcium phosphate were added. SAN copolymer was prepared by suspension polymerization by washing, dehydrating and drying the resultant product. SAN copolymer in powder form was obtained.

(D-1) A mixture of t-butyl substituted monophosphate esters

A mixture of t-butyl substituted monophosphate esters containing 0.5% by weight of triphenyl phosphate, 33.2% by weight of diphenyl (t-butylphenyl) phosphate, 49.5% by weight of phenyl di(t-butylphenyl) phosphate and 12.5% by weight of tri(t-butylphenyl) phosphate was used.

(D-2.1) Monomeric phosphate ester

Triphenyl phosphate (TPP) of Daihachi Co. of Japan was used.

(D-2.2) Oligomeric phosphate ester

Resorcinoldiphosphate(RDP) with an average M value of 1.3 in Formula (II) was used.

(E) Fluorinated polyolefin

Polytetrafluoroethylene with an average particle size of 10-50㎛ was used.

EXAMPLES 1-4 AND COMPARATIVE EXAMPLES 1-4

Eight different thermoplastic resin compositions were prepared from the above -mentioned constituents in the amount as indicated in the following Table 1 and the properties of the compositions were also shown in Table 1. The indicated constituents were mixed with an antioxidant and a thermal stabilizer, and then compounded in a twin-screw extruder(L/D 29, Φ=45). The resulting extrudates were pelletized and the test pieces were injection-molded from the pellets at the temperature of 220-280℃ and maintained at 23℃, 50% RH before measuring the properties.

The thermoplastic resin compositions of Examples 1 to 4 were those comprising a mixture of t-butyl substituted monophosphate esters(D-1), and a monomeric phosphate ester (D2.1) or an oligomeric phosphate ester (D2.2). The thermoplastic resin compositions of Comparative Examples 1 to 4 are those having the same compositions with the composition of example 1 but as a flame retardant containing only a monophosphate ester compound, an oligomeric phosphate ester compound or both, respectively.

TABLE 1

EXAMPLE NO.	EXAMPLES				COMPARATIVE EXAMPLES			
	1	2	3	4	1	2	3	4
COMPOSITIONS (parts by weight)								
(A) Polycarbonate	80	80	80	80	80	80	80	80
(B) Graft copolymer (g-ABS)	10	10	10	10	10	10	10	10

(C) SAN	10	10	10	10	10	10	10	10
(D-1) A mixture of t-buyl substituted monophostphates	7	3	7	3	-	-	-	-
(D-21) TPP	3	7	-	-	10	-	7	3
(D-22) RDP	-	-	3	7	-	10	3	7
(E) Fluorinated polyolefin(7AJ)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
PROPERTIES								
Heat Resistance (VST, ℃)[1]	100	97	103	102	93	99	96	97
Number of cracks[2]	3	7	2	6	31	24	19	13
Total length of the cracks (mm) [3]	13.5	35.4	11.3	33.7	235.5	194.7	150.5	89.3

TEST METHOD

[1] Heat resistance was determined according to ASTM D306.

[2] Determined by measuring the number of the cracks generated following the storage for 24 hours in the oven at the temperature of 80℃ after injection molding the test pieces by a box-shaped mold.

[3] Determined by measuring the total length of the cracks generated following the storage for 24 hours in the oven at the temperature of 80℃ after injection molding the test pieces by a box-shaped mold.

EXAMPLES 5-11 AND COMPARATIVE EXAMPLES 5-8

Thermoplastic resin compositions having a composition as shown in Table 2 and Table 3 were prepared by the same method with Example 1-4 and the measured properties were also shown in Table 2 and Table 3.

TABLE 2

EXAMPLE NO.	EXAMPLES.						
	5	6	7	8	9	10	11
COMPOSITIONS (parts by weight)							
(A) Polycarbonates	80	80	80	80	80	80	80
(B) Graft polymer (g-ABS)	10	10	10	10	10	10	10
(C) SAN	10	10	10	10	10	10	10
(D-1) A mixture of t-butyl substituted monophosphates	10	8	8	6	6	4	4
(D-2.1) TPP	-	2	-	4	-	6	-
(D-2.2) RDP	-	-	2	-	4	-	6
(E) Fluorinated polyolefin(7AJ)	0.4	0.4	0.4	0.4	0.4	0.4	0.4
PROPERTIES							
Heat Resistance (VST, ℃)	105	103	104	101	103	98	102
Number of cracks	1	3	2	6	5	11	7
Total length of the cracks	5.3	13.5	11.3	33.7	29.6	53.1	36.7

TABLE 3

EXAMPLE NO.	COMPARATIVE EXAMPLES			
	5	6	7	8
COMPOSITIONS (parts by weight)				
(A) Polycarbonates	80	80	80	80
(B) Graft copolymer (g-ABS)	10	10	10	10
(C) SAN	10	10	10	10
(D-1) A mixture of t-butyl substituted monophosphates	-	-	-	-
(D-2.1) TPP	8	2	6	4

(D-2.2) RDP	2	8	4	6
(E) Fluorinated polyolefin (7AJ)	0.4	0.4	0.4	0.4
PROPERTIES				
Heat Resistance (VST, ℃)	95	99	97	96
Number of cracks	28	18	25	23
Total length of the cracks	124.3	103.2	117.6	110.8

As shown in Tables 1 and 2, examples 1-4 and 5-11 showed improved heat resistance and drastic reduction in number and length of the cracks. By contrast, comparative examples 1-4 and 5-8 showed poor heat resistance and increased number and length of the cracks. As can be seen from the results of Tables 1, 2 and 3, the thermoplastic resin compositions according to the invention, which contain as a flame retardant, a mixture of alkyl substituted monophosphate esters, and a monomeric phosphate ester or an oligomeric phosphate ester showed distinctly higher stress cracking resistance and improved heat resistance than those of the comparative examples with only monomeric phosphate ester(Comparative Example 1), only oligomeric phosphate ester(Comparative Example 2) or a mixture of monomeric phosphate ester and oligomeric phosphate ester (Comparative Examples 3-8).

Consequently, these results show that stress cracking resistance and heat resistance of the thermoplastic resin compositions according to the present invention are subtantially improved by a combination of flame retardants comprising a mixture of alkyl substituted monophosphate esters and a phosphate ester compound.

CLAIMS:

1. A thermoplastic resin composition comprising:

(A) 40 to 95 parts by weight of a halogen-free, thermoplastic polycarbonate;

(B) 5 to 50 parts by weight of a styrene-containing graft copolymer prepared by grafting (B-1) onto (B-2):

(B-1) 5 to 95% by weight, based on (B), of a mixture of :

(B-1.1) 50 to 100% by weight of styrene, α-methyl styrene, ring-substituted styrene, methyl methacrylate or a mixture thereof, and

(B-1.2) 50 to 0% by weight of acrylonitrile, methacrylonitrile, C_1-C_8 alkyl methacrylate, C_1-C_8 alkyl acrylate, alkyl acrylate, maleic anhydride, N-substituted maleimide or a mixture thereof;

(B.2) 95 to 5% by weight, based on (B), of a rubber with a glass transition temperature(Tg) of below -10℃ and selected from the group consisting of butadiene rubbers, acryl rubbers, ethylene/propylene rubbers, styrene/butadiene rubbers, acrylonitrile/butadiene rubbers, butadiene/styrene rubbers, polyisoprene, EPDM rubbers, polyorganosiloxane, and mixtures thereof;

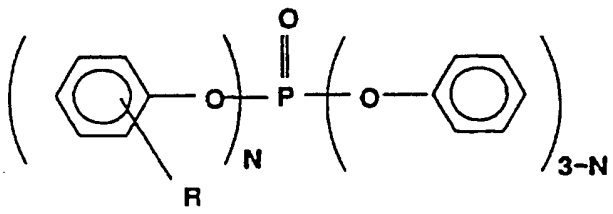
(C) 0 to 30 parts by weight of a styrene containing copolymer prepared from:

(C-1) 50 to 95% by weight of styrene, α-methyl styrene, ring-substituted styrene, methyl methacrylate or a mixture thereof, and

(C-2) 50 to 5% by weight of acrylonitrile, C_1-C_8 alkyl methacrylate, C_1-C_8 alkyl acrylate, or a mixture thereof;

(D) 5 to 20 parts by weight, based on 100 parts by weight of (A)+(B)+(C), of a mixture comprising:

(D-1) 100 to 5 % by weight of a mixture of alkyl substituted monophosphate esters of the formula (I):



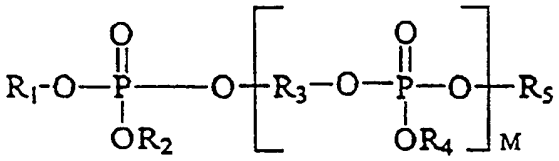
(I)

in which:

R is an alkyl group selected from t-butyl, isopropyl, isobutyl, isoamyl, t-amyl, and

N is 0 or an integer from 1 to 3; and

(D-2) 0 to 95 % by weight,of phosphate esters of the formula (II):



(II)

in which;

R_1, R_2, R_4, and R_5 are independently cresyl, phenyl, xylenyl, propylphenyl, butylphenyl, or brominated or chlorinated derivatives thereof,

R_3 is an arylene group, and

M is 0 to 5; and

(E) 0 to 2 parts by weight, based on 100 parts by weight of (A)+(B)+(C), of a fluorinated polyolefin polymer.

2. A thermoplastic resin composition according to claim 1, wherein said component (D-1) is a mixture comprising by weight:

1 to 20% of the alkyl-substituted monophosphate ester wherein N is 3,

10 to 50% of the alkyl-substituted monophosphate ester wherein N is 2,

15 to 60% of the alkyl-substituted monophosphate ester wherein N is 1, and

less than 2% triphenyl phosphate.

3. A thermoplastic resin composition according to claim 1, wherein the weight ratio of (D-1) to (D-2) is between 80:20 and 5:95.

4. A thermoplastic resin composition according to claim 1, wherein the weight ratio of (D-1) to (D-2) is between 55:45 and 15:85.

5. A thermoplastic resin composition according to claim 1, wherein said alkyl group(R) is t-butyl.

6. A thermoplastic resin composition according to claim 1, wherein said alkyl group(R) is isopropyl.

7. A thermoplastic resin composition according to claim 1, wherein said component (D-1) is a mixture of the mixed t-butyl substituted monophosphate esters and the mixed isopropyl substituted monophosphate esters.

8. A thermoplastic resin composition according to claim 1 or claim 2, wherein said resin composition further includes at least one additive selected from the group consisting of inorganic fillers, glass fibers, carbon fibers, thermal stabilizers, antioxidants, light stabilizers, plasticizers, mold release agents, pigments, and dyes.

9. A thermoplastic resin composition according to claim 2, wherein said component (D-1) is a mixed t-butyl substituted monophosphate ester composition comprising by weight:

1 to 20% tri(t-butylphenyl) phosphate,

10 to 50% di(t-butylphenyl) phosphate,

15 to 60% diphenyl (t-butylphenyl) phosphate and

less than 2% triphenyl phosphate.

10. A thermoplastic resin composition according to claim 1, substantially as described herein with reference to the Examples.

The Patent Office

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Application No:	GB 9817271.1	**Examiner:**	Miss M M Kelman
Claims searched:	1 to 10	**Date of search:**	13 October 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C3K KEC KEF KEZ

Int Cl (Ed.6): C08K 5/00, 5/521, 5/523

Other: ONLINE: CLAIMS, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
Y	EP 0731140 A2	CHEIL see the claims and page 4, line 25	1,2,5,6,7, 8,9
Y	EP 0324716 A2	CIBA-GEIGY see whole document	1,5,6,7,8
Y	US 5672645 A	BAYER see the claims and column 8, line 14	1,2,5,6,7, 8,9
Y	US 5206404 A	FMC CORPORATION see the claims and column 3, line 43	1,2,5,6,7, 8,9
Y	US 5204394 A	GENERAL ELECTRIC see the claims and Examples C,D,E and F	1,2,5,6,7, 8,9

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.